

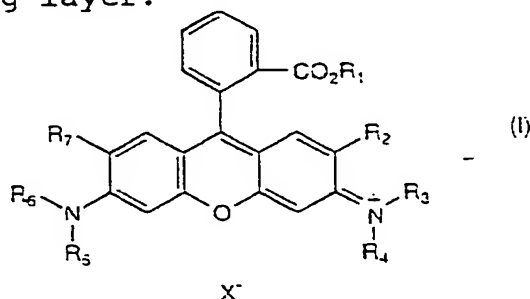
Laid-Open Number: 11-58977
 Laid-Open Date: Mar. 2, 1999
 Application Number: 9-243461
 Application Date: Aug. 25, 1997
 IPC's: B41M 5/26, C09B 11/28, G11B 7/24
 Applicant: TDK Corp.
 Inventors: E. Kanbe, A. Kadota and M. Niimi
 Title: Optical Recording Medium

page 13:
 Dialkylamino

[Abstract]

An optical recording medium of heat mode system that has sufficient solubility to a coating solution invading no polycarbonate substrate and excellent recording and reproduction characteristics by means of light of wavelengths of 680 nm or less.

In the optical recording medium having a recording layer and a reflection layer where the wavelengths of recording and/or reproducing light is 680 nm or less, a Rhodamine dye represented by the following formula (I) is contained in the recording layer:

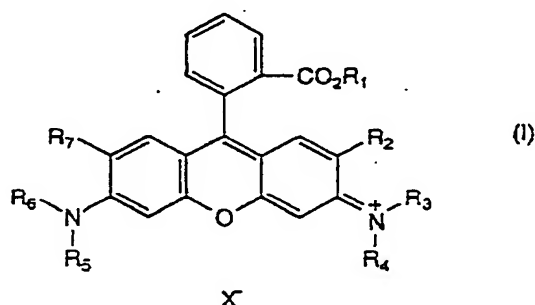


[In formula (I) R₁ represents a hydrogen atom or an alkyl group

having one to four carbon atoms. R_1 through R_n , independently represent a hydrogen atom or an alkyl group or an alkoxy group having one to four carbon atoms. X^- represents a counter anion.]

[Claims]

[Claim 1] An optical recording medium wherein wavelengths of recording and/or reproducing light are 680 nm or less and the medium has a recording layer containing a dye on a substrate, has a reflection layer on the recording layer and forms pits by irradiation with light to carry out recording, the medium being characterized in that the recording layer contains a dye represented by the following formula (I):



[In formula (I) R_1 represents a hydrogen atom or an alkyl group having one to four carbon atoms. R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 independently represent a hydrogen atom or an alkyl group or an alkoxy group having one to four carbon atoms. X^- represents a counter anion.]

[Claim 2] An optical recording medium as described in claim 1 wherein the counter anion represented by X^- in formula (I) is an organic metal complex anion.

[Claim 3] An optical recording medium as described in claims 1 or 2 the recording layer further contains an organic

metal complex dye.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to an optical recording medium that has a reflection layer and preferably forms pits by irradiation with laser light and particularly, to an optical recording medium where the recording and reproducing wavelengths are from 600 to 680 nm.

[0002]

[Prior Art]

The recording method of the optical recording medium used practically at present is a heat mode recording method where vaporization or decomposition is produced in the recording layer by irradiation with laser light as a heat source to form concave pits that are optically detectable.

[0003] On the other hand, as another recording method that encounters many problems and fails to come into practical use, Japanese Patent Laid-Open Nos. 308439/1990 and 6204/1996 propose a photon mode recording method where a recording layer containing various fluorescent substances is irradiated with light to provide and record physical and chemical changes and in reproduction, emission from the recording layer is detected.

[0004] The organic dye type recording layers of the heat

mode optical recording medium have hitherto contained as one of dyes cyanine dyes, which however are markedly deteriorated by light to lack stability. In addition, azo dyes also are exemplified, which have high resistance to light, but have the disadvantage of low reflectance.

[0005]

[Problems that the Invention is to Solve]

An object of the invention is to provide an optical recording medium having excellent recording-reproducing characteristics to have sufficient solubility to a coating solvent without invading a polycarbonate substrate and exhibit good jitters with light of wavelengths of 680 nm or less. Another object of the invention furthermore is to provide an optical recording medium having excellent resistance to light.

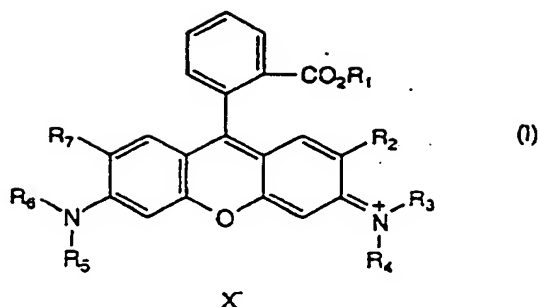
[0006]

[Means for Solving the Problems]

The objects can be achieved according to the following items (1) through (3):

(1) An optical recording medium where the wavelengths of recording and/or reproducing light are 680 nm or less and the medium has a recording layer containing a dye on a substrate, has a reflection layer on the recording layer, and forms pits by irradiation with light to perform recording, the optical recording medium being characterized in that the recording layer contains a dye represented by formula (I):

[0007]



[0008] [In formula (I) R_1 represents a hydrogen atom or an alkyl group having one to four carbon atoms. R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 independently represent a hydrogen atom, or an alkyl group or an alkoxy group having one to four carbon atoms. X^- represents a counter anion.]

(2) An optical recording medium as described in the above item (1) wherein the counter anion represented by X^- in formula (I) is an organic metal complex anion.

(3) An optical recording medium as described in items (1) or (2) wherein the recording layer further contains an organic metal complex dye.

[0009] Japanese Patent Laid-Open Nos. 308439/1990 and 6204/1996 disclose a optical recording medium where the recording layer contains Rhodamine 6G, Rhodamine B, etc. that are included in the dyes represented by formula (I). The optical recording medium disclosed therein, however, is an optical recording medium utilizing a photon mode where the presence or absence of fluorescence emitted from a recording

layer is detected to carry out the recording and reproduction of information, which is apparently different from the optical recording medium of the invention where recording utilizes a heat mode and in reproduction, the difference between reflectances is detected.

[0010]

[Mode for Carrying Out the Invention]

The invention is hereinafter illustrated in detail. In the optical recording medium of the invention, the wavelengths of recording and/or reproducing light is 680 nm or less. The medium is of a heat mode where a reflection layer is formed on a recording layer and small holes called pits are formed by irradiation with light to conduct recording. The recording layer contains Rhodamine dyes represented by formula (I).

[0011] In formula (I), R_1 represents a hydrogen atom or an alkyl group having one to four carbon atoms; R_2 through R_7 each represent a hydrogen atom, an alkyl group having one to four carbon atoms, or an alkoxy group having one to four carbon atoms; and X^- represents a counter anion.

[0012] The alkyl group having one to four carbon atoms represented by R_1 through R_7 can be either of a straight chain or of a branched chain. Examples thereof include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, and t-butyl. These groups can have substituent groups. Examples of such substituent groups include an alkoxy group such as methoxy and

ethoxy, an alkoxy carbonyl group, a hydroxy group, hydroxyoxy (hydroperoxy) group, and a halogen atom, etc. Even when a substituent group is contained, the number of carbon atoms preferably is from one to four.

[0013] The alkoxy group having one to four carbon atoms represented by R_2 through R_7 can be either of a straight chain or of a branched chain in the alkyl moiety. Examples thereof include methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, s-butoxy, and t-butoxy. Although an alkoxy group containing no substituent group is preferred, the group may further be substituted. Even when a substituent group is contained, the number of carbon atoms preferably is from one to four.

[0014] R_1 is preferably a hydrogen atom or a non-substituted alkyl group (methyl or ethyl).

[0015] R_2 and R_7 each are preferably a hydrogen atom, a non-substituted alkyl group (methyl or ethyl), or a non-substituted alkoxy group (methoxy or ethoxy).

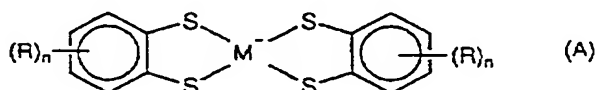
[0016] R_3 through R_6 each are preferably a hydrogen atom or an alkyl group (methyl, ethyl, propyl, butyl, and ethoxyethyl). At least one of R_3 and R_4 and at least one of R_5 and R_6 are preferably an alkyl group.

[0017] Examples of the counter anion represented by X^- include halide ions (Cl^- , Br^- , I^- , etc.), ClO_4^- , BF_4^- , PF_6^- , VO_3^- , VO_4^{3-} , WO_4^{2-} , $CH_3SO_3^-$, CF_3COO^- , CH_3COO^- , HSO_4^- , $CF_3SO_3^-$, $PO_4 \cdot 12WO_3^{3-}$,

p-toluenesulfonate ion (PTS^-), and p-trifluoromethylphenylsulfonate ion (PFS^-), etc. Of these, Cl^- , Br^- , ClO_4^- , and BF_4^- , etc. are preferred.

[0018] In addition, anions of organic metal complexes are preferably exemplified. Such organic metal complexes include those known as metal complex quenchers. Examples thereof include anions of metal complexes of acetylacetonate type, bisdithiol type such as bisdithio- α -diketone type and bisphenylenedithiol type, thiocatechol type, salicylaldehyde oxime type, and thiobisphenolate type. Of these, anions of metal complexes of bisphenylenedithiol type are preferred. Preferred anions of metal complexes of bisphenylenedithiol type are those represented by the following formula (A):

[0019]



[0020] In formula (A), M represents a central metal that includes Ni, Cu, Co, Pd, Pt, etc. Ni and Cu are preferred. R represents an alkyl group, an alkoxy group, an alkyl-substituted amino group, or a halogen atom. n is an integer of one to four.

[0021] The alkyl group represented by R can be either of a straight chain or of a branched chain and preferably has one to four carbon atoms, including methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, s-butyl, and t-butyl, etc. The

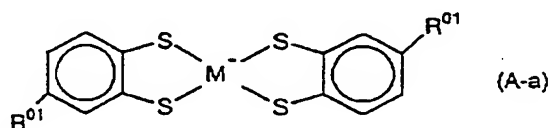
alkoxy group preferably has one to four carbon atoms and includes methoxy and ethoxy, etc. The alkylamino group preferably has one to four carbon atoms in the alkyl moiety and is preferably a di-substituted amino group, etc. A dibutylamino group is exemplified. The halogen atom is exemplified by Cl, etc.

[0022] n is an integer of one to four and preferably an integer of one to three.

[0023] Examples of anions represented by formula (A) are herein shown. The invention is not to be construed as being limited by these.

In the following, pursuant to the expression of formula (A-a), etc., combinations of M, R⁰¹, etc. are given.

[0024]

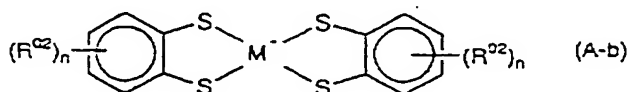


A-1: M=Cu R⁰¹=t-C₄H₉

A-2: M=Ni R⁰¹=t-C₄H₉

A-3: M=Cu R⁰¹= —N(C₄H₉)₂

A-4: M=Cu R⁰¹= —OCH₃



A-5: M=Ni R⁰²=Cl n=3

A-6: M=Cu R⁰²=Cl n=3

A-7: M=Ni R⁰²=Cl n=2

[0025] Anions of phenylazophenyl metal complexes are further exemplified and anions of metal complexes between azo compounds represented by the following formula (B-I) and metals are preferred. The metal complexes containing the azo compounds represented by formula (B-I) as ligands are those having a quenching function.



[0027] In formula (B-I), Q_1 and Q_2 each represent an aromatic group that has a group containing active hydrogen in a position adjacent to the diazo group.

[0028] Formula (B-I) is illustrated in more detail. The aromatic rings of the aromatic rings groups represented by Q_1 and Q_2 that have a group containing active hydrogen can be either of carbon rings or of heterocycles and can be monocyclic, fused polycyclic, or ring-collective polycyclic. Examples of such aromatic rings include a benzene ring, a naphthalene ring, a pyridine ring, a thiazole ring, a benzothiazole ring, an oxazole ring, a benzoxazole ring, a quinoline ring, an imidazole ring, a pyrazine ring, and a pyrrole ring, etc. Of these, the benzene ring, the naphthalene ring and the pyrrole ring are preferred and the benzene ring is particularly preferred.

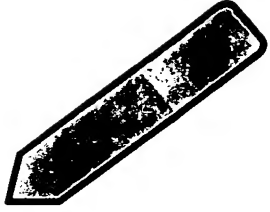
[0029] Combinations of Q_1 and Q_2 are preferably those of two benzene rings, benzene ring-naphthalene ring, and benzene ring-pyrrole ring, etc. Of these, a combination of two benzene

rings is most preferred.

[0030] The linking position of the group having active hydrogen in the aromatic rings represented by Q_1 and Q_2 is a position adjacent to the diazo group. Examples of the groups having active hydrogen include $-OH$, $-SH$, $-NH_2$, $-COOH$, $-CONH_2$, $-SO_2NH_2$, and $-SO_3H$, etc. Of these, the group $-OH$ is particularly preferred.

[0031] The aromatic rings represented by Q_1 and Q_2 can contain further substituent groups as well as an azo group and a group having active hydrogen. Examples of the substituent groups include a nitro group, a halogen atom (e.g., chlorine atom and bromine atom, etc.), a carboxyl group, a sulfo group, a sulfamoyl group (preferably, zero to four carbon atoms; e.g., sulfamoyl and methylsulfamoyl, etc.), an alkyl group (preferably, one to four carbon atoms; e.g., methyl, etc.), and an amino group, etc.

[0032] When Q_1 and Q_2 are a benzene ring, respectively, one of the benzene rings preferably contains a nitro group or a halogen atom (preferably, chlorine atom and bromine atom) as a substituent group and the nitro group is particularly preferred. The nitro group and the halogen atom are preferably present in the meta or the para position to the diazo group and particularly, the presence in the meta position is preferred. Two or more substituent groups, which are the same or different, can be contained therein. The other benzene ring



preferably contains an amino group as a substituent group. The amino group can be a non-substituted amino group, but particularly preferably a dialkylamino group. The dialkylamino group preferably has two to eight carbon atoms in total. Examples thereof include a dimethylamino group, a diethylamino group, a methylethylamino group, a methylpropylamino group, a dibutylamino group, and a hydroxyethylmethylamino group, etc. The position of such amino groups substituted is preferably the para position to the diazo group.

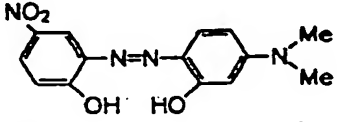
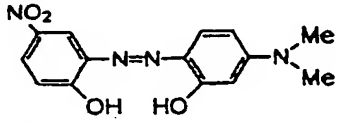
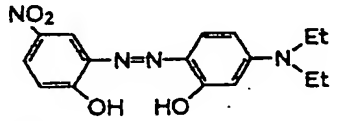
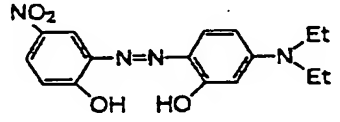
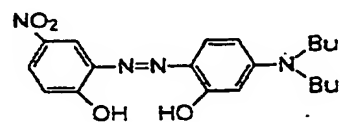
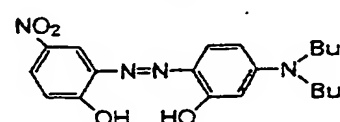
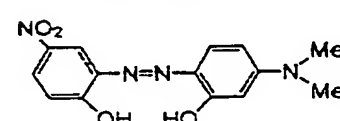
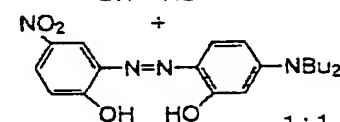
[0033] The central metals of the metal complexes prepared from azo compounds of formula (B-I) as ligands must form anions without counter ions. The central metals are Co, vanadyl ($V=O$), etc. and form complexes with an azo compound (as Ligands) in ratio of azo compound to metal of 2:1. In this case, the ligands may be the same or different.

[0034] The groups having active hydrogen of formula (B-I) coordinate to the central metals in the form of acid anions (When the group having active hydrogen is $-OH$, the form is $-O^-$).

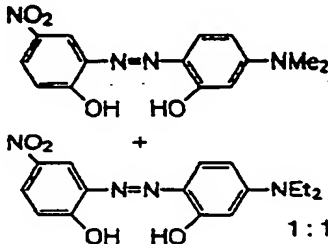
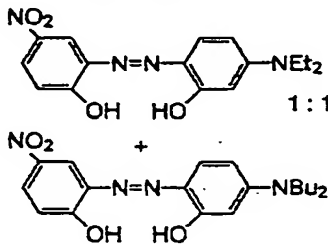
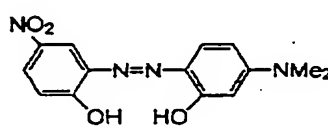
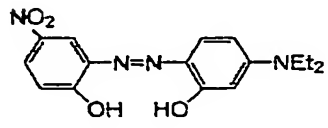
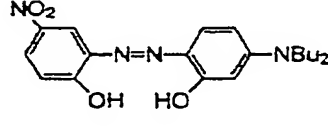
[0035] Examples of the anions represented by formula (B-I) are shown below, but the invention is not limited by these examples. These anions are herein shown in combinations of azo compounds and central metals. The ratio of ligand to metal is 2:1. Metal complexes of the examples are all univalent anions. Metal complexes having two central metals are

mixtures of metal complex anions containing the respective metals as central metals. Me, Et, and Bu in the examples represent methyl, ethyl and butyl, respectively.

[0036]

Anion	Ligand	Central Metal
B-I-1		Co
B-I-2		V = O
B-I-3		Co
B-I-4		V = O
B-I-5		Co
B-I-6		V = O
B-I-7		Co
	 1:1	

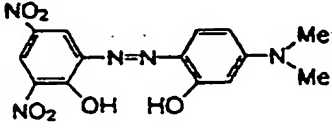
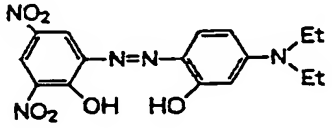
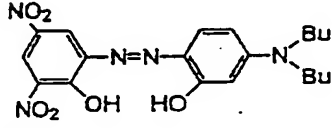
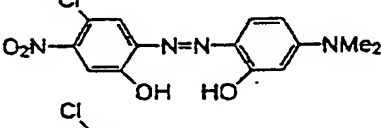
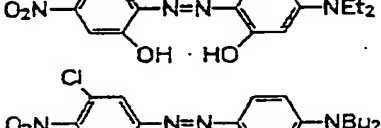
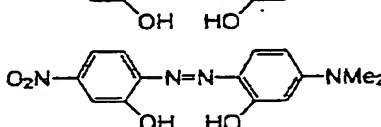
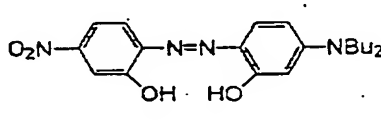
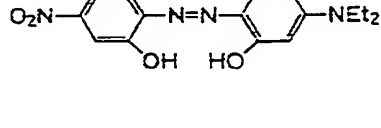
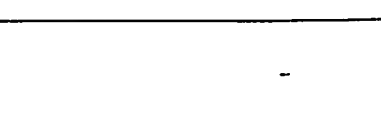
[0037]

Anion	Ligand	Central Metal
B + 8		Co
B + 9		Co
B + 10		Co+V=O 1:1
B + 11		Co+V=O 1:1
B - 12		Co+V=O 1:1

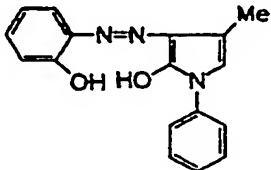
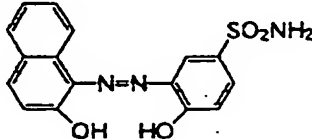
[0038]

Anion	Ligand	Central Metal
B -I-13		Co
B -I-14		Co
B -I-15		Co
B -I-16		Co
B -I-17		Co
B -I-18		Co
B -I-19		Co
B -I-20		Co
B -I-21		Co

[0039]

Anion	Ligand	Central Metal
B -I-22		Co
B -I-23		Co
B -I-24		Co
B -I-25		Co
B -I-26		Co
B -I-27		Co
B -I-28		Co
B -I-29		Co
B -I-30		Co

[0040]

Anion	Ligand	Central Metal
B-I-31		Co
B-I-32		Co

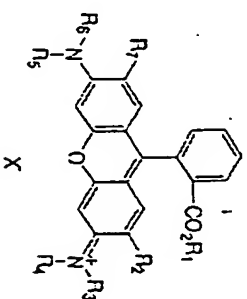
[0041] The organic metal complex anions are particularly preferred as anions.

[0042] Of these organic metal complex anions, the phenylazophenyl complex anions are particularly preferred in order to acquire optical constants necessary to characteristics of the optical recording medium.

[0043] Rhodamine dyes of general formula (I) used in the invention are shown below, but the present invention is not to be construed as being limited by these. The indications in formula (I) are herein followed. When X^- is an organic metal complex anion, the indications exemplified before are followed. Me, Et, Pr, and Bu represent methyl, ethyl, propyl, and butyl, respectively.

[0044]

Dye	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇	X
I-1	H	H	Et	Et	Et	Et	H	Cl ⁻
I-2	Et	Me	Et	H	Et	H	Me	ClO ₄ ⁻
I-3	H	Me	Et	H	Et	H	Me	Cl ⁻
I-4	Et	H	Et	Et	Et	Et	H	Br ⁻
I-5	H	H	Pr	Pr	Pr	Pr	H	Cl ⁻
I-6	Et	H	Bu	Bu	Bu	Bu	H	ClO ₄ ⁻
I-7	H	Et	Et	H	Et	H	Et	Cl ⁻
I-8	Et	MeO	Et	H	Et	H	MeO	Cl ⁻
I-9	Et	H	EIOEt	H	EIOEt	H	MeO	Cl ⁻
I-10	H	H	Et	Et	Et	Et	H	B-I-1
I-11	Et	Me	Et	H	Et	H	Me	B-I-2
I-12	H	Me	Et	H	Et	H	Me	B-I-3
I-13	Et	H	Et	Et	Et	Et	H	B-I-4
I-14	H	H	Pr	Pr	Pr	Pr	H	B-I-31
I-15	Et	H	Bu	Bu	Bu	Bu	H	B-I-1
I-16	H	Et	Et	H	Et	H	Et	B-I-2
I-17	Et	MeO	Et	H	Et	H	MeO	B-I-3
I-18	Et	H	EIOEt	H	EIOEt	H	MeO	B-I-4



(II)

[0045] The Rhodamine dyes of formula (I) are commercially available and can be synthesized according to known procedures.

[0046] In order to obtain the azo dyes having organic metal complex anions, the corresponding ClO_4^- salts or BF_4^- salts are synthesized and thereafter, anions are exchanged by known methods by use of organic metal complex salts according to the desired organic metal complex anions.

[0047] Melting points (mp) of the Rhodamine dyes of the invention are from 220 to 350°C and λ_{max} 's (measured as dye films of 50 nm thickness) are in the range of from 500 to 610 nm.

[0048] In the wavelength of 635 nm or 650 nm, the real part (n) of the complex refractive index is from 2.0 to 2.50 and the imaginary part (k) thereof is from 0.03 to 0.10.

[0049] The n's and k's of the dyes are calculated as follows. A dye film is provided on a certain transparent substrate in thickness almost similar to the recording layer of the optical recording medium, for example, in thickness of about 40 to about 100 nm, under the same conditions as the recording layer, thus to prepare a sample for measurement. Subsequently, the reflectances and the transmissions of the sample for measurement are measured at 635 nm or 650 nm. The values (n and k) are calculated from the measurements thus obtained according to a method as described, for example, in K. Ishiguro, Kogaku, p.168-178, Kyoritsu Zensho. The reflectance is that by allowing to passing through the substrate of the sample for

measurement or that from the dye film side and is measured through specular reflection (about 5°).

[0050] The Rhodamine dyes in the invention can be used singly or in combination with two or more thereof as dyes for the recording layer.

[0051] These dyes have excellent resistance to light, sufficient solubility to organic solvents, and increased solubility to coating solvents that fail to invade polycarbonate resins (PC) widely used as substrate materials for the optical recording medium.

[0052] The recording layers containing these dyes are preferably used for a postscript type optical recording disk (DVD-R) in particular. This recording layer can be provided by use of a coating solution containing the dye. Spin coating where the coating solution is developed and coated on a revolving substrate is particularly preferred. In addition, gravure coating, spray coating, and dipping can be applied.

[0053] After spin coating as described above, the film is dried as needed. The thickness of the recording layer thus formed is appropriately set according to a desired reflectance, etc., but in general is from 500 to 3000 angstroms.

[0054] The content of the dyes in the coating solutions is preferably from 0.05 to 10 weight percent in general. Since the solubility of the azo dyes of the invention is good, the coating solution having such content can be easily prepared.

Concretely, the azo dyes in the invention exhibit good solubility to polar solvents and 0.5 to 10 weight percent of the azo dyes is dissolved in alcohols, cellosolves, alkoxyalcohols, ketoalcohols such as diacetone alcohol, ketone such as cyclohexanone, and fluorinated alcohols such as 2,2,3,3-tetrafluoropropanol. One weight percent or more of the dyes is dissolved in ethyl cellosolve or 2,2,3,3-tetrafluoropropanol that are suitable solvents for coating polycarbonate disk substrates and it is possible to make high-quality spin coating films in a short time.

[0055] A binder, a dispersant, a stabilizer, and the like can be appropriately contained in the coating solutions.

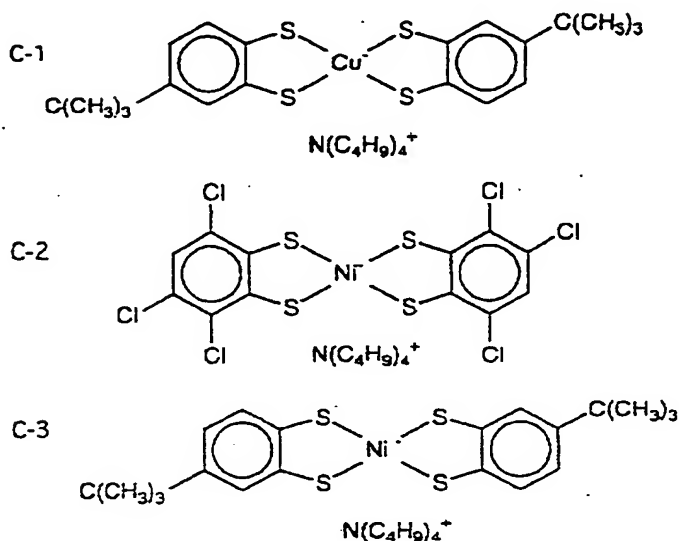
[0056] In addition to the dyes of the invention, other light absorbing dyes can be contained in the recording layer of the optical recording medium of the invention. Examples of such dyes indicate cyanine dyes, metal complex dyes different from the dyes as described above, styryl dyes, polyphiline dyes, azo dyes different from the azo dyes as described above, and formazan metal complexes. In this case, such dyes are contained in the coating solutions and a recording layer can be prepared.

[0057] Such dyes include salts of the organic metal complex anions that are the counter anions as described above. About salts of the anions of formula (A), for example, ammonium ions such as tetrabutylammonium ion and alkali metal ions such as

Na⁺ and K⁺ are preferred as the counter cations to form the salts.

[0058] Examples of such organic metal complexes that are the salts of formula (A) are shown below.

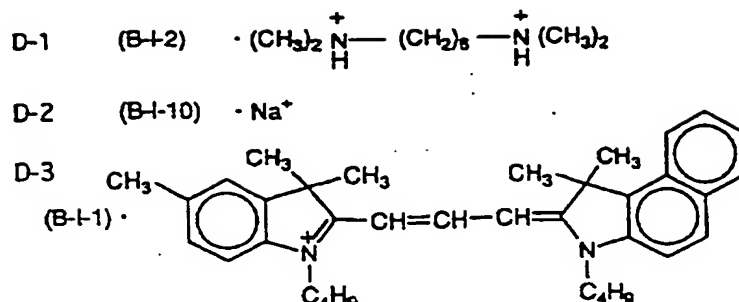
[0059]



[0060] Moreover, salts of the anions of metal complexes having the azo compounds of formula (B-I) as ligands also are included. The counter cations of this case are inorganic cations such as Na⁺, Li⁺ and K⁺, ammonium ions represented by R¹¹R¹²R¹³R¹⁴N⁺ (Herein, R¹¹, R¹², R¹³, and R¹⁴ each are a hydrogen atom, an alkyl group, or an alkoxy group, etc.), and R¹¹R¹²R¹³N⁺-(CH₂)_k-N⁺R¹³R¹²R¹¹ (Herein, R¹¹, R¹², and R¹³ each represent a hydrogen atom, an alkyl group, an alkoxy group, etc. and k is 5 to 10).

[0061] Examples of the organic metal complexes that are the salts of formula (B-I) are shown below.

[0062]



[0063] Furthermore, metal complexes having as ligands the azo compounds represented by formula (B-II) similar to formula (B-I) also are preferred.

[0064]



[0065] In formula (B-II), Q_3 represents an aromatic rings group having active hydrogen in a position adjacent to the diazo group and Q_4 represents a nitrogen-containing hetero-aromatic rings group having the nitrogen atom capable of coordinating to a metal atom in a position adjacent to the carbon atom to which the azo group links.

[0066] Formula (B-II) is illustrated in more detail. The aromatic rings group represented by Q_3 that has active hydrogen has the same meanings as Q_1 and Q_2 in formula (B-I).

[0067] The nitrogen-containing hetero-aromatic rings group represented by Q_4 that has a nitrogen atom capable of coordinating to a metal atom can be of unicycle or of fused polycycle. Examples of such nitrogen-containing hetero-

aromatic rings preferred include a pyridine ring, a thiazole ring, a benzothiazole ring, an oxazole ring, a benzoxazole ring, a quinoline ring, an imidazole ring, a pyrazine ring, and a pyrrole ring, etc. Of these, the pyridine ring, the quinoline ring, and the thiazole ring are more preferred. The position of the nitrogen atom in a ring is a position adjacent to the carbon atom to which the diazo group links. These can have substituent groups similarly to Q_1 and Q_2 .

[0068] Preferred combinations of Q_3 and Q_4 include those of a benzene ring and a pyridine ring, a benzene ring and a thiazole ring, and a benzene ring and a quinoline ring, etc.

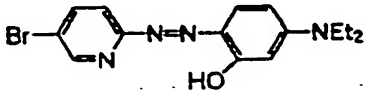
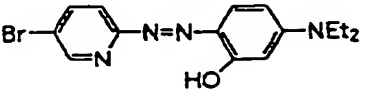
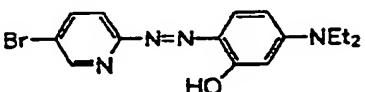
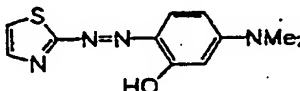
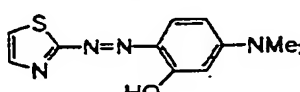
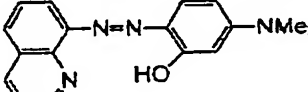
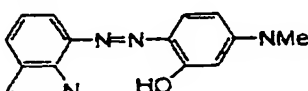
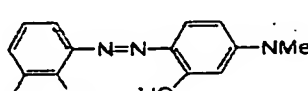
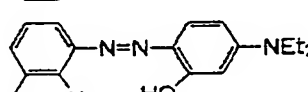
[0069] Co, vanadyl, Ni, and Cu are preferred as the central metals of these metal complexes.

[0070] The metal complexes themselves are compounds having no charge or positive charge according to the central metals. When the compounds have positive charge, the counter ions are anions similar to the counter anions as shown in X^- of formula (I), including halide ions (e.g., Cl^- , Br^- and I^- , etc.), ClO_4^- , and BF_4^- , etc.

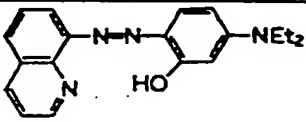
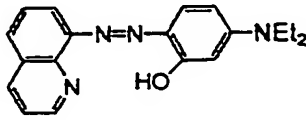
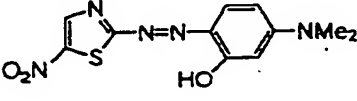
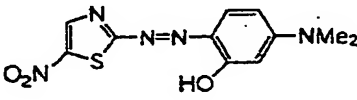
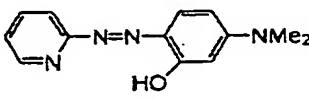
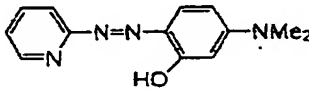
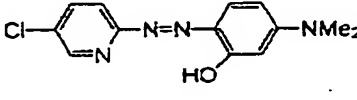
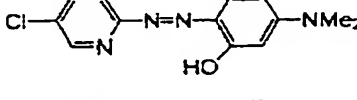
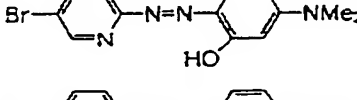
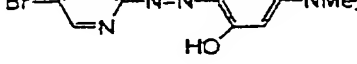
[0071] Other things are similar to the case of formula (B-I).

[0072] Examples of these metal complexes are shown below in combination of azo compounds and central metals.

[0073]

Anion	Ligand	Central Metal
B-II-1		Cu
B-II-2		Ni
B-II-3		Co
B-II-4		Ni
B-II-5		Cu
B-II-6		Co
B-II-7		Ni
B-II-8		Cu
B-II-9		Co

[0074]

Anion	Ligand	Central Metal
B-II-10		Ni
B-II-11		Cu
B-II-12		Cu
B-II-13		Ni
B-II-14		Cu
B-II-15		Ni
B-II-16		Cu
B-II-17		Ni
B-II-18		Cu
B-II-19		Ni

[0075] The metal complexes as described above all are compounds having a quencher function.

[0076] These compounds can be used singly or in combination of two or more thereof.

[0077] When the counter anions of the dyes of formula (I) are not the anions of organic metal complexes, addition of these organic metal complexes in particular is effective in more improvement in resistance to light.

[0078] The ratio of the dyes of formula (I) to the organic metal complexes is preferably from 3:1 to 1:3 in molar ratio.

[0079] The coating solvents used in the invention can be appropriately selected from alcohols (including ketoalcohols and alkoxyalcohols such as ethylene glycol monoalkyl ethers, etc.), aliphatic hydrocarbons, ketones, esters, ethers, aromatics, halogenated alkanes, etc.

[0080] Of these, alcohols, aliphatic hydrocarbons, etc. are preferred. Of the alcohols, alkoxyalcohols, ketoalcohols, etc. are preferred. In the alkoxyalcohols, the number of carbon atoms in alkoxy moieties is preferably from one to four, the number of carbon atoms in alcohol moieties is preferably from one to five and more preferably from two to five, and the total number of carbon atoms in molecules is preferably from three to seven. Examples thereof include ethylene glycol monoalkyl ethers (cellosolves) such as ethylene glycol monomethyl ether (i.e., methyl cellosolve), ethylene glycol

monoethyl ether (i.e., ethyl cellosolve or ethoxyethanol), butyl cellosolve, and 2-isopropoxy-1-ethanol, 1-methoxy-2-propanol, 1-methoxy-2-butanol, 3-methoxy-1-butanol, 4-methoxy-1-butanol, and 1-ethoxy-2-propanol, etc. An example of the ketoalcohols is diacetone alcohol, etc. Furthermore, fluorinated alcohols such as 2,2,3,3-tetrafluoropropanol, etc. also are usable.

[0081] Preferred examples of the aliphatic hydrocarbons include n-hexane, cyclohexane, methylcyclohexane, ethylcyclohexane, cyclooctane, dimethylcyclohexane, n-octane, iso-propylcyclohexane, and t-butylcyclohexane, etc. and of these, ethylcyclohexane and dimethylcyclohexane, etc. are preferred.

[0082] The ketones are exemplified by cyclohexanone, etc.

[0083] In the invention, the alkoxyalcohols of ethylene glycol monoalkyl ether type are preferred and above all, ethylene glycol monoethyl ether, 1-methoxy-2-propanol, and 1-methoxy-2-butanol, etc. are preferred. Furthermore, mixed solvents comprising these alkoxyalcohols also are usable and include, for example, a combination of ethylene glycol monoethyl ether and 1-methoxy-2-butanol. Fluorinated alcohols also are preferably used.

[0084] The constitution of a postscript type digital video disk (DVD-R) to perform recording and reproduction at a short wavelength of about 635 nm or about 650 nm, which is a preferred

embodiment of the optical recording medium of the invention, is shown as an example in Fig. 1. Fig. 1 is a partial sectional view.

[0085] As shown in Fig. 1, optical recording disk 10 is an optical recording disk corresponding to standards on DVD, which is formed by laminating protective film 15 and protective film 25 of two disks having similar structures. The thickness of adhesive layer 50 is from about 10 to about 200 μm . In this case, the thickness of a substrate (in general, polycarbonate resins) is 0.6 mm per sheet. Recording layer 13, reflection layer 14, and protective layer 15 are successively formed on substrate 12 that has groove 123 and on the other hand, recording layer 23, reflection layer 24, and protective layer 25 are similarly formed on substrate 22 that has groove 223. Both disks are laminated as described above, thus to form disk 10. For the lamination, a hot-melt adhesive agent, a delayed UV adhesive agent or an adhesive sheet is utilized.

[0086] Substrate 12 or 22 is disk-like in shape and can be formed of a resin or glass substantially transparent (preferably a transmission of 88 percent or more) to recording light and reproducing light (laser rays of wavelengths of from about 600 to about 680 nm, further from about 630 to about 680 nm, particularly from about 635 to about 680 nm, and most particularly 635 nm or 650 nm) in order to enable recording and reproduction from the Back surface side of substrate 2.

The size of the substrates is from about 64 to about 200 mm in diameter and about 0.6 mm in thickness.

[0087] Groove 123 or 223 for tracking is produced in planes formed by substrate 12 or 22 and recording layer 13 or 23 as shown in Fig. 1. Groove 123 or 223 is preferably a spiral continuous groove, which is preferably from 0.05 to 0.20 μm (from 500 to 2000 angstroms) in depth, from 0.20 to 0.40 μm in width, and from 0.65 to 0.85 μm in groove pitch. Such structure of the groove makes it possible to obtain a good tracking signal without reduction in reflection level of the groove. It is particularly important to regulate the width of the groove to from 0.20 to 0.40 μm . The width of the groove less than 0.2 μm makes it difficult to obtain a sufficiently large tracking signal and a slight offset of tracking on recording tends to produce large jitters. A large width of the groove tends to produce waveform distortion.

[0088] Resins are preferably used as materials of substrate 12 or 22 and a wide variety of thermoplastic resins such as polycarbonate resins, acryl resins, amorphous polyolefin, TPX, and polystyrene resins are appropriately used. The substrate can be prepared by use of such resins according to known processes such as injection molding. Groove 123 or 223 is preferably formed on molding substrate 12 or 22. After preparing substrate 12 or 22, a resin layer having groove 123 or 223 can also be formed by the 2P method. In some cases,

a glass substrate can also be used.

[0089] As shown in Fig. 1, recording layer 13 or 23 provided onto substrate 12 or 22 is that formed by use of the dye-containing coating solution as described above preferably by spin coating as described above. The spin coating can be carried out at ordinary conditions from inside to outside by adjusting the number of revolutions to from 500 to 5000 rpm.

[0090] The thickness of recording layer 13 or 23 thus formed is from 50 to 300 nm (from 500 to 3000 angstroms) and in complex refractive indexes at wavelengths of recording and reproducing light, the real part (n) is from 2.0 to 2.8 and the imaginary part (k) is less than 0.4.

[0091] The thickness exceeding the range as described above results in reduction in reflectance, which makes it difficult to carry out good reproduction.

[0092] The regulation of n and k enables good recording and reproduction as described above. The k exceeding 0.4 fails to produce sufficient reflectance. The n less than 2.0 brings about too small modulation degrees of signals. The upper limit of n is not particularly limited, but usually about 2.8 for some reason in syntheses of dye compounds.

[0093] In order to find n and k of the recording layer, a recording layer is provided onto a certain transparent substrate under practical conditions, for example, so as to be from about 40 to about 100 nm in thickness to prepare a sample

for measurement and subsequently, the reflectance from the substrate side of the sample or the reflectance from the recording layer side thereof are measured. In this case, the reflectance is measured by use of the wavelength of reflecting and reproducing light (635 or 650 nm) through specular reflection (about 5°). The transmission of the sample is further measured. The n and k can be calculated from these measurements according to a method, for example, as described in K. Ishiguro, Kogaku, p. 168-178, Kyoritsu Zensho.

[0094] Reflection layer 14 or 24 is provided adhesively onto recording layer 13 or 23 as shown in Fig. 1. Metals or alloys having high reflectances such as Au, Cu, Al, Ag, and AgCu are preferably used as reflection layer 14 or 24. The thickness of reflection layer 14 or 24 is preferably 50 nm (500 angstroms) or more and such a layer can be provided through deposition or sputtering. The upper limit of the thickness is not particularly limited, but preferably about 120 nm (1200 angstroms) or less in view of costs and an operation time for production. This ensures that the reflectance of a single reflection layer 14 or 24 is 90 percent or more, which is sufficient as reflectance from non-recording portion side of the substrate of the medium.

[0095] Protective layer 15 or 25 is provided onto reflection layer 14 or 24 as shown in Fig. 1. Protective layer 15 or 25 is formed of a variety of resin materials, for example,

ultraviolet-curing resins so as to be from about 0.5 to about 100 μm in thickness. Protective layer 15 or 25 can be layer-like or sheet-like. Protective layer 15 and 25 can be formed by usual methods such as spin coating, gravure coating, spray coating, or dipping.

[0096] In order to carry out a recording or postscript on optical recording disk 1 having such structure, the disk is irradiated with recording light of, for example, 635 or 650 nm as a pulse through substrate 12 or 22 to change the reflectance of irradiated portions. When irradiated with the recording light, recording layer 13 or 23 absorbs light to generate heat and substrate 12 or 22 also is heated at the same time. As a result, in the proximity of the interface of substrate 12 or 22 and recording layer 13 or 23, melting or decomposition arises in materials such as dyes in the recording layer to produce pressure in the proximity of the interface between recording layer 13 and substrate 12 or between recording layer 23 and substrate 22, which may deform the bottom or the side wall of the groove.

[0097]

[Examples]

The invention is illustrated through examples together with comparative examples in more detail.

[0098] Example 1:

A recording layer containing a dye was formed so as to

be 1000 angstroms (100 μm) in thickness through spin coating by use of dye I-1 as a dye for the optical recording layer onto a polycarbonate resin substrate with a diameter of 120 mm and a thickness of 0.6 mm that had a pregroove (0.12 μm in depth, 0.30 μm in width, and 0.74 μm in groove pitch). The coating solution used was 1.0 weight percent solution in 2,2,3,3-tetrafluoropropanol. Subsequently, an Au reflection layer with a thickness of 850 angstroms was formed on the recording layer by sputtering and a transparent protective film (thickness 5 μm) was further formed of an ultraviolet-curing acrylic resin. Two disks thus prepared were laminated with an adhesive with the two protective films facing inward, thus to prepare a disk (see Fig. 1).

[0099] This disk is termed sample No. 1.

[0100] Similarly to sample No. 1, samples were prepared except that respective dyes or mixtures of dyes as shown in Table 1 were used as dyes for the recording layer in place of dye I-1 (see Table 1).

[0101] In samples No. 10 through 16, dye mixtures were used so that the ratio of dyes of formula (I) (I-1, I-2, and I-8) to organic metal complexes (C-1 through C-3, D-1 through D-3, and B-II-2) was 7:3 in molar ratio.

[0102] About the samples thus prepared, a signal was recorded by means of a laser ray of 635 nm at a linear speed of 3.5 m/s and reproduced by means of a laser ray of 650 nm

at a linear speed of 3.5 m/s to evaluate characteristics of the samples. The aperture of lens (NA) was 0.60. Reflectance in 650 nm, modulation degree (14TMod.), jitter, optimum recording power (Po) in 635 nm were evaluated as the characteristics.

[0103] Results are shown in Table 1.

[0104]

Table 1

Sample No.	Dye	Reflectance (%)	Mod. (%)	Jitter (%)	PO (mW)
1	I-1	50	65	7.3	9.1
2	I-2	48	66	7.1	9.2
3	I-3	55	64	7.2	9.3
4	I-4	53	68	7.6	9.2
5	I-5	52	64	7.5	9.6
6	I-6	53	66	7.9	9.5
7	I-7	55	68	6.8	9.3
8	I-8	55	69	7.6	9.5
9	I-9	56	63	8.1	9.4
10	I-1+C-1	59	66	8	9.2
11	I-2+C-2	53	68	8.2	9.3
12	I-1+C-3	50	63	7.6	9
13	I-1+D-1	55	66	8	8.0
14	I-2+D-2	54	63	8.3	8.3
15	I-8+D-3	52	63	8.5	8.8
16	I-1+B-II-2	50	63	8.0	8.9
17	I-10	49	64	7.5	10.3
18	I-11	53	61	7.1	9.6
19	I-12	54	63	7.2	9.9
20	I-13	51	63	7.3	9.3
21	I-14	52	63	7.4	9.9
22	I-15	56	69	7.2	9.4
23	I-16	55	65	7.3	9.8
24	I-17	59	66	7.1	9.6
25	I-18	55	66	7	9.6

[0105] As may be seen from Table 1, all samples has been found to present good results about reflectance, modulation

degree, and jitter.

[0106] About samples No. 1 through 25, furthermore, resistance to light was examined. In order to examine the resistance to light, the samples were irradiated with a xenon lamp of 80,000 luxes (Xenon fadeometer manufactured by Shimadzu Corp.) for 40 hours to check the jitters of the disks.

[0107] As a result, about samples No. 10 through 25, the changes in jitter were small. About samples No. 1 through 9, the changes in jitter were large as compared with those of samples No. 10 through 25, but exhibited better levels than a sample in the following Comparative Example 1 where a trimethinecyanine dye is used. Good results were obtained particularly in samples No. 17 through 25 where salt-forming dyes were used. The jitter did not change at all in the samples where dyes that contain counter anions having preferred structures (I-10 through I-13 and I-15 through I-18) were used.

[0108] About samples No. 1 through 25, furthermore, a reliability test was carried out under conditions of 80°C-80%RH and 100 hours.

[0109] As a result, samples No. 17 through 25 caused no deterioration in characteristics. Samples No. 1 through 16 produced large deterioration in characteristics, but exhibited better levels than the sample of Comparative Example 1 where a trimethinecyanine dye was used.

[0110] Comparative Example 1:

[0111]

CC1=C(C)C(=C2C=CC=CC=C2N1C4CCCC4)C=CC=C/C=C/C5=C(C)C(=C6C=CC=CC=C6N5C7CCCC7)C8=CC=CC=C8.[O-]P(=O)(Cl)Cl

According to the invention, an optical recording medium exhibiting excellent balance among recording sensitivity, reflectance and modulation degree, high recording sensitivity and small jitter is obtained by use of highly soluble Rhodamine dyes as light-absorbing layers. Use of the salt-forming dyes containing Rhodamine dye cations and organic metal complex anions as the Rhodamine dyes in particular produces improvement in resistance to light and reliability.

[Fig. 1] Fig. 1 is a partial sectional view showing an example of the optical disks of the invention.

[Description of the Reference Numerals]

10:	Optical Recording Disk
12, 22:	Substrate
123, 223:	Groove
13, 23:	Recording Layer
14, 24:	Reflection Layer
15, 25:	Protective Film
50:	Adhesive Layer